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14. ABSTRACT New measurements have been made of rate constants for electron attachment to $c\text{-C}_4\text{F}_8$ (octafluorocyclobutane) and thermal electron detachment from the parent anion, $c\text{-C}_4\text{F}_8^-$ , over the temperature range 298–400 K in 133 Pa of He gas in a flowing-afterglow Langmuir-probe apparatus. From these data the electron affinity for $c\text{-C}_4\text{F}_8$ was determined, $\text{EA}(c\text{-C}_4\text{F}_8) = 0.63 \pm 0.05$ eV. The motivation was to resolve a discrepancy between our earlier EA estimate and a higher value ( $\text{EA} = 1.05 \pm 0.10$ eV) reported from a recent experiment of Hiraoka <i>et al.</i> [J. Chem. Phys. 116, 7574 (2002)]. The electron attachment rate constant is $9.3 \pm 3.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at 298 K. The electron detachment rate constant is negligible at room temperature but climbs to $1945 \pm 680 \text{ s}^{-1}$ at 400 K. G3(MP2) calculations were carried out for the neutral ( $D_{24}$ , $^1\text{A}_1$ ) and anion ( $D_{44}$ , $^2\text{A}_{2u}$ ) and yielded $\text{EA}(c\text{-C}_4\text{F}_8^-) = 0.595$ eV. Bond energies were also calculated for loss of F from $c\text{-C}_4\text{F}_8$ and loss of F or $\text{F}^-$ from $c\text{-C}_4\text{F}_8^-$ . From these, dissociative electron attachment is found to be endothermic by at least 1.55 eV. © 2004 American Institute of Physics.			
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# Electron attachment and detachment and the electron affinity of cyclo- $C_4F_8$

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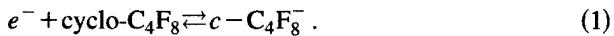
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## I. INTRODUCTION

Electron attachment to  $c\text{-}C_4F_8$  (octafluorocyclobutane) has been shown to yield  $C_4F_8^-$  over a broad range of electron energies below 200 meV.<sup>1</sup> An electron spin resonance study showed that the  $C_4F_8$  ion product is cyclic.<sup>2</sup> A decade ago we measured<sup>3</sup> rate constants for electron attachment to  $c\text{-}C_4F_8$  and electron detachment from  $c\text{-}C_4F_8^-$  in 133 Pa of He gas over the temperature range 300–375 K, as represented by the following equation:



From these data an equilibrium constant was obtained and yielded an estimate of the electron affinity  $EA(c\text{-}C_4F_8) = 0.63$  eV. No uncertainty was specified at the time because certain assumptions had to be made to deduce  $EA(c\text{-}C_4F_8)$  from the measured free energy of attachment,  $\Delta G^0$ . The entropy change in the reaction was estimated by assuming that the internal motions of neutral and anionic  $c\text{-}C_4F_8$  were approximately the same in order to obtain the reaction enthalpy  $\Delta H^0$ , and that the integrated specific heats of neutral and anionic  $c\text{-}C_4F_8$  were approximately the same in order to obtain EA from  $\Delta H^0$ . However,  $\Delta G^0$  was considered accurate to  $\pm 0.02$  eV, and we felt that our value of  $EA(c\text{-}C_4F_8)$  was certainly good to within  $\pm 0.10$  eV.

So it was with some surprise to read of a pulsed high-pressure mass spectrometry measurement (in 400 Pa  $N_2$  gas at 150–350 K) of charge-transfer equilibrium between  $SF_6$  and  $c\text{-}C_4F_8$  which gave  $EA(c\text{-}C_4F_8) = 1.05 \pm 0.10$  eV,<sup>4</sup> that is, the same as  $SF_6$  itself.<sup>5</sup> Had an isomer of  $c\text{-}C_4F_8^-$  of  $EA > 1$  eV existed in our flow tube experiment, that isomer would not have detached the extra electron at a measurable rate even at our highest temperature of 550 K. We had seen no evidence of nondetaching anions. Hiraoka *et al.* found a different isomer  $c\text{-}C_4F_8^{*-}$  of low detachment energy in charge-transfer equilibrium between  $O_2$  and  $c\text{-}C_4F_8$  over the temperature range 260–455 K, and the electron binding energy for this supposedly higher-lying isomer of the anion was measured to be  $0.52 \pm 0.05$  eV. Hiraoka *et al.* also carried out density functional calculations which appeared to support their measurement of  $EA(c\text{-}C_4F_8) = 1.05$  eV. Hiraoka *et al.* were apparently unaware of our earlier work.<sup>3</sup>

This matter is of importance in that  $c\text{-}C_4F_8$  is a common feedstock for plasma etching of silicon dioxide in semiconductor manufacturing. If the plasma temperature were to be even 50 C, significant electron detachment would occur from  $c\text{-}C_4F_8^-$  if the electron binding energy lies in the 0.5–0.6 eV range, but insignificant if in the 1 eV neighborhood. In addition, Morris *et al.*<sup>6</sup> have shown that the electron attachment process limits the lifetime of  $c\text{-}C_4F_8$  in the earth's atmosphere, provided that electron attachment destroys the parent

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molecule, either in the attachment process or because of subsequent ion-molecule reactions. The reactivity of *c*-C<sub>4</sub>F<sub>8</sub><sup>-</sup> may depend on its electron binding energy. (Atmospheric temperatures are too low for thermal detachment to occur.) The dielectric strength of *c*-C<sub>4</sub>F<sub>8</sub> has also been studied to evaluate its use as an insulating gas in high-voltage devices.<sup>7</sup>

We have revisited the *c*-C<sub>4</sub>F<sub>8</sub> problem with a number of improvements in the methodology. (1) The gas temperature is now constant in the interaction zone of the apparatus, within 1–2 K, as detailed later, following tests which showed that the buffer gas required a longer distance to equilibrate with the walls of the apparatus than appreciated at the time of our earlier work. (2) Gas flow meters, which measure the reactant concentration, are now regularly calibrated for He. (3) It is now possible to routinely calculate the entropy and heat capacity corrections that are needed for converting the attachment/detachment equilibrium constant (measured at elevated temperature) into a reaction enthalpy at 0 K. (4) In our earlier work, we assumed that *c*-C<sub>4</sub>F<sub>8</sub><sup>-</sup> had the same symmetry as does *c*-C<sub>4</sub>F<sub>8</sub>, which we now know to be incorrect as a result of the calculations reported here. The change in the rotational symmetry number affects EA(*c*-C<sub>4</sub>F<sub>8</sub>) by 18 meV.

Thus, we are able to measure the electron attachment rate constants,  $k_a$ , and the electron detachment rate constants,  $k_d$ , more accurately than a decade ago, and we are able to interpret the results in terms of EA(*c*-C<sub>4</sub>F<sub>8</sub>) more accurately. The bottom line is that we are able to give an accurate value for the adiabatic electron affinity of *c*-C<sub>4</sub>F<sub>8</sub>,  $0.63 \pm 0.05$  eV. This result suggests that one of the experiments of Hiraoka *et al.*<sup>4</sup> is wrong, probably because SF<sub>6</sub><sup>-</sup> has been found not to be a good electron-transfer agent.<sup>5</sup> Further, we feel that Hiraoka *et al.* should not have taken their calculated (density functional) result as confirming their measured EA. It is our experience<sup>8,9</sup> that density functional calculations tend to yield a value of the EA that is too large, by an amount (0.2–0.5 eV) depending on the size of the basis set. We have carried out density functional calculations in the present work along with more accurate G3(MP2) ones. EA(*c*-C<sub>4</sub>F<sub>8</sub>) obtained using the G3(MP2) method<sup>10</sup> adds evidence that the high value of EA(*c*-C<sub>4</sub>F<sub>8</sub>) measured by Hiraoka *et al.*<sup>4</sup> is incorrect. On the other hand, the electron detachment results and *c*-C<sub>4</sub>F<sub>8</sub><sup>-</sup>/O<sub>2</sub><sup>-</sup> equilibrium data of Hiraoka *et al.*<sup>4</sup> are consistent with the present results.

## II. EXPERIMENTAL METHOD

A flowing-afterglow Langmuir-probe (FALP) apparatus was used for this work at the Air Force Research Laboratory. Both the method<sup>11</sup> and this particular apparatus<sup>12</sup> have been well-described in the literature and will not be detailed here, aside from the temperature issue discussed earlier. The measurements were carried out in 133 Pa of He gas. The *c*-C<sub>4</sub>F<sub>8</sub> gas<sup>13</sup> was introduced into the flow tube at a concentration of typically 400 ppmv. An example of the data obtained is shown in Fig. 1. Data such as these were fit to determine  $k_a$  and  $k_d$  as described in Ref. 1. Results at each temperature are given in Table I.

Originally, the gas temperature in our FALP apparatus

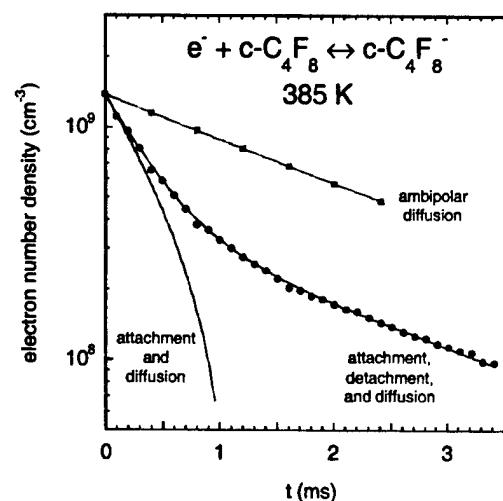


FIG. 1. An example of the FALP data for *c*-C<sub>4</sub>F<sub>8</sub> at 385 K, with a concentration of *c*-C<sub>4</sub>F<sub>8</sub> of  $1.81 \times 10^{11}$  cm<sup>-3</sup>. The upper solid line was obtained without *c*-C<sub>4</sub>F<sub>8</sub> and gave  $\nu_D = 470$  s<sup>-1</sup>. The fit to the lower data set yielded  $k_a = 8.8 \times 10^{-9}$  cm<sup>3</sup> s<sup>-1</sup> and  $k_d = 1105$  s<sup>-1</sup>.

was measured only with a thermocouple at the wall of the flow tube halfway along the interaction region. Five years ago a thermistor was mounted on the movable Langmuir probe, and temperature measurements were made along the axis of the FALP flow tube. It was found that the flowing He gas was not completely temperature-equilibrated by the time the gas reached the reactant inlet port, which lies halfway along the 1 m length of the flow tube. The gas temperature could be lower than thought, by as much as 10 K. While  $k_a$  values rarely change rapidly with temperature,  $k_d$  rates change nearly exponentially with temperature. Presently, the heating of the flow tube is divided into three separately

TABLE I. Rate constants for electron attachment to *c*-C<sub>4</sub>F<sub>8</sub> and electron detachment from *c*-C<sub>4</sub>F<sub>8</sub><sup>-</sup>. The experimental uncertainty is  $\pm 35\%$  except that the  $k_d$  in parentheses are not reliable since they are smaller than the ambipolar diffusion rate (but give the best fit to the data). For comparison with  $k_d$ , the measured ambipolar diffusion decay constant  $\nu_D$  is given for the electron-(He<sup>+</sup>, Ar<sup>+</sup>) plasma at 133 Pa pressure and  $\sim 100$  m s<sup>-1</sup> plasma velocity. The calculated [B3LYP/6-311+G(3df)] entropy  $S^0$  and integrated specific heat  $\int C_p dT$  are given in plain type for *c*-C<sub>4</sub>F<sub>8</sub> and in italics for *c*-C<sub>4</sub>F<sub>8</sub><sup>-</sup>.

<i>T</i> (K)	$k_a$ ( $10^{-9}$ cm <sup>3</sup> s <sup>-1</sup> )	$k_d$ (s <sup>-1</sup> )	$\nu_D$ (s <sup>-1</sup> )	$S^0$ (meV K <sup>-1</sup> )	$\int C_p dT$ (meV)	EA (meV)
298	9.1	(15)	335	...	...	...
	9.5	(15)	335	...	...	...
313	8.5	(30)	351	...	...	...
	8.7	(145)	357	...	...	...
349	8.4	(290)	393	...	...	...
	8.2	(285)	393	...	...	...
361	8.1	470	414	4.533	382.0	614
	9.0	510	414	4.650	410.8	615
373	8.0	745	458	4.594	403.5	620
	8.4	755	458	4.717	434.2	621
385	8.8	1105	470	4.655	425.3	631
	8.0	1125	470	4.782	458.0	627
	9.3	1120	457	...	...	632
	9.3	1155	457	...	...	631
	9.0	1945	472	4.729	453.2	637
				4.862	488.3	

TABLE II. Results of Møller-Plesset and density functional calculations for  $D_{2d}(^1A_1)c\text{-C}_4\text{F}_8$  and  $D_{4h}(^2A_{2u})c\text{-C}_4\text{F}_8^-$ .

Quantity	G3(MP2)		DFT	
	$c\text{-C}_4\text{F}_8$	$c\text{-C}_4\text{F}_8^-$	$c\text{-C}_4\text{F}_8$	$c\text{-C}_4\text{F}_8^-$
Zero-point energy <sup>a</sup>	0.047 49	0.041 20	0.046 43	0.040 10
Total energy (0 K) <sup>b</sup>	-950.198 61	-950.220 49	-951.146 91	-951.181 52
EA (eV) <sup>b</sup>	0.595	...	0.942	...
$r(\text{C-C})$ (Å) <sup>c</sup>	1.550 <sup>e</sup>	1.489	1.579 <sup>e</sup>	1.505
$r(\text{C-F})$ (Å) <sup>c</sup>	1.340	1.489	1.334	1.406
$r(\text{C-F})$ (Å) <sup>c</sup>	1.350	1.489	1.339	1.406
Dihedral (degrees) <sup>d</sup>	17.1 <sup>e</sup>	0.0	8.0 <sup>e</sup>	0.0

<sup>a</sup>HF/6-31G(d) level of theory, scaled by 0.8929, for G3(MP2) results and B3LYP/6-31+G(3df) level of theory, scaled by 0.989, for DFT results, in hartree units.

<sup>b</sup>G3(MP2) formalism and B3LYP/6-31+G(3df)//B3LYP/6-31+G(3df)+ZPE for DFT results, in hartree units.

<sup>c</sup>MP2(full)/6-31G(d) for G3(MP2) results and B3LYP/6-31+G(3df) for DFT results; in the puckered  $c\text{-C}_4\text{F}_8$  ring, alternating C-F bonds have different bond lengths.

<sup>d</sup>The C-C-C-C dihedral angle indicates the amount of pucker in the  $c\text{-C}_4\text{F}_8$  ring.

<sup>e</sup>An electron diffraction experiment (Ref. 24) gave  $r(\text{C-C})=1.566\pm 0.008$  Å and a dihedral angle of  $17.4^\circ \pm 0.3^\circ$ .

temperature-controlled zones, with the upstream zone receiving additional heating to get the He gas up to operating temperature well ahead of the reactant inlet port, which is near the middle of the second heating zone. The efficiency of the present heating system, using the movable, axial thermistor, shows the temperature constant to within 1–2 °C at all temperatures in the 298–550 K range. The temperature is measured with three miniature resistance-temperature-detector devices mounted inside the flow tube.

We also regularly obtain calibrations of the gas flow meters<sup>14</sup> by timing the flow of He gas into a known volume. The concentration of  $c\text{-C}_4\text{F}_8$  in the flow tube is determined from the relative throughputs and the total gas pressure. The  $c\text{-C}_4\text{F}_8$  reactant was prepared in mixtures of typically 1% in helium in order to allow a readily measurable flow rate to be used. We note that  $k_d$ , a unimolecular rate constant, is not dependent on the  $c\text{-C}_4\text{F}_8$  concentration. We also measure  $k_a$  for SF<sub>6</sub> at room temperature for comparison with the benchmark result of Crompton *et al.*<sup>15</sup>

As outlined in Ref. 3, and illustrated in Fig. 1, the electron density plot reaches a diffusion-limited steady-state at long times if  $k_d$  is greater than the ambipolar diffusion decay constant  $\nu_D$ . If a nondetaching anion is produced in the attachment process, even with a branching fraction of a few percent, the electron density drops away from the steady-state line shown in Fig. 1, at a rate dependent upon the branching fraction. The optimum temperatures (373–385 K in this experiment) for determining  $k_d$  are those for which  $k_d$  is larger than the ambipolar diffusion decay constant  $\nu_D$  (the latter being measured in absence of reactant gas), but not so large as to dominate the attachment frequency  $\nu_a=k_a n_r$ . For this reason, values of  $\nu_D$  are included in Table I for comparison to  $k_d$ . (Values of  $\nu_D$  may vary in different experiments because of the small amount of Ar gas added to the He.) These considerations mean that  $k_d$  cannot be determined reliably at low temperatures (298–349 K in this experiment). The fitted values of  $k_a$  and  $k_d$  depend only on relative values of the electron density as long as the initial electron number

density is much greater than the reactant concentration,  $n_r$ , at the reactant port.

### III. COMPUTATIONAL METHOD

Computations were carried out for neutral (point group  $D_{2d}$ , puckered carbon ring, rotational quantum number 4) and anionic (point group  $D_{4h}$ , planar carbon ring, rotational quantum number 8)  $c\text{-C}_4\text{F}_8$  using the GAUSSIAN-03W program package.<sup>16</sup> EA( $c\text{-C}_4\text{F}_8$ ) was computed using the G3(MP2) method, which is accurate *on average* within 56 meV.<sup>10</sup> The hybrid density functional B3LYP<sup>17,18</sup> was used with the 6-31+G(3df) Gaussian basis set to compute entropy and heat capacity quantities needed to interpret the attachment/detachment results in terms of EA( $c\text{-C}_4\text{F}_8$ ). The stability of the wave functions was checked; i.e., the molecular orbital set chosen was verified to be the lowest-energy set. The results of the calculations are given in Tables I and II. The density functional method is expected to give better entropies and heat capacities (Table I), partly because it is feasible to utilize a larger basis set than used for the frequency analysis in the G3(MP2) method. On the other hand, the G3(MP2) method will give a better value for EA( $c\text{-C}_4\text{F}_8$ ), certainly within 0.1 eV. The density functional method used here tends to give EAs about 0.25 eV too high.<sup>8,9</sup>

G3(MP2) calculations were also carried out on  $c\text{-C}_4\text{F}_7$  neutral and anionic fragments in order to determine the threshold for dissociative electron attachment. The calculated (C<sub>4</sub>F<sub>7</sub>-F) bond energy is 4.974 eV at 0 K, and the bond enthalpy is 5.021 eV at 298 K. The calculated (C<sub>4</sub>F<sub>7</sub>-F<sup>-</sup>) bond energy is 2.158 eV at 0 K, and the bond enthalpy is 2.188 eV at 298 K. The calculated (F-C<sub>4</sub>F<sub>7</sub><sup>-</sup>) bond energy is 2.396 eV at 0 K, and the bond enthalpy is 2.428 eV at 298 K. EA( $c\text{-C}_4\text{F}_7$ ) = 3.173 eV. These figures indicate that dissociative electron attachment to  $c\text{-C}_4\text{F}_8$  is endothermic by at least 1.55 eV at 298 K.

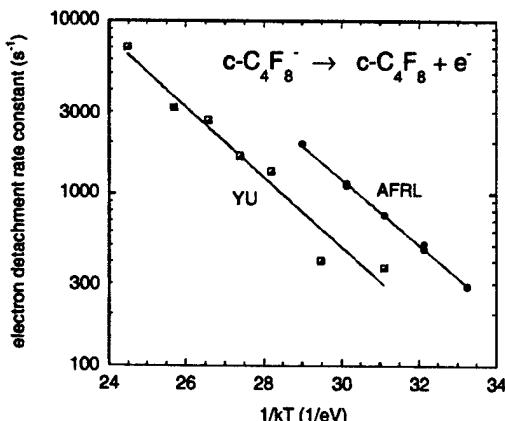


FIG. 2. Electron detachment rate constants vs  $1/kT$ . AFRL: present data. YU: data from Ref. 4 (Yamanashi University). The solid lines are from Eq. (2) using,  $k_a = 9.0 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  with entropy and heat capacities listed in Table I, and  $\text{EA}(c\text{-C}_4\text{F}_8) = 0.63 \text{ eV}$  for the AFRL data, and  $\text{EA}(c\text{-C}_4\text{F}_8) = 0.68 \text{ eV}$  for the YU data.

#### IV. RESULTS

The measured values of  $k_a$  and  $k_d$  are given in Table I. The electron attachment rate constant is  $9.3 \pm 3.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  at 298 K. The electron detachment rate constant is negligible at room temperature but increases nearly exponentially to  $1945 \pm 680 \text{ s}^{-1}$  at 400 K.

As shown in Refs. 3 and 9, the  $k_d$  follow a temperature dependence given by

$$k_d = k_a L_0 (273.15/T) \exp[-(\text{EA}/kT) - (\Delta S^0/k) - (H_T - H_0)/kT]. \quad (2)$$

In Eq. (2),  $k$  is Boltzmann's constant,  $L_0$  is Loschmidt's number, EA is the electron affinity of *c*-C<sub>4</sub>F<sub>8</sub> (at 0 K, by definition),  $\Delta S^0$  is the entropy change due to electron attachment, and  $H_T - H_0$  is the thermal energy correction needed to reduce the EA result to 0 K. The  $T$  dependence of  $k_d$  is thus complicated by that contained implicitly in other quantities such as  $k_a$  and the heat capacities of the neutral and anion. The electron part of the entropy term  $\Delta S^0$  in the argument of the exponential contributes a factor of  $T^{5/2}$  to  $k_d$ . In the present case,  $k_a$  changes very little in the narrow temperature range accessible to us. Figure 2 shows the present  $k_d$  data along with those of Hiraoka *et al.*<sup>4</sup> Both sets of data are consistent with a low value of EA(*c*-C<sub>4</sub>F<sub>8</sub>).

EA(*c*-C<sub>4</sub>F<sub>8</sub>) may be obtained from the measured  $k_a$  and  $k_d$  using the inverse of Eq. (2), with details given in Ref. 3 in terms of  $\Delta G^0$  and  $\Delta H^0$ . An example will be given for the 385 K data, using one set of measured values from Table I:  $k_a = 9.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  and  $k_d = 1155 \text{ s}^{-1}$ . The B3LYP/6-31+G(3df) DFT calculations yielded entropy and integrated heat capacity values for *D*<sub>2d</sub> *c*-C<sub>4</sub>F<sub>8</sub> and *D*<sub>4h</sub> *c*-C<sub>4</sub>F<sub>8</sub><sup>-</sup> as listed in Table I. The entropy change is

$$\Delta S^0 = S(\text{anion}) - S(\text{neutral}) - S(\text{electron}), \quad (3)$$

$$\Delta S^0 = 4.782 - 4.655 - 0.273 \text{ meV K}^{-1} \text{ at } 385 \text{ K} \quad (4)$$

for a net entropy change of  $-0.146 \text{ meV K}^{-1}$ , or  $T\Delta S^0 = -56 \text{ meV}$ . The integrated heat capacities needed to convert the "EA" at 385 K to a true EA (at 0 K) are

$$H_T - H_0 = \int_0^T C_p(\text{electron}) dT + \int_0^T C_p(\text{neutral}) dT - \int_0^T C_p(\text{anion}) dT, \quad (5)$$

$$H_T - H_0 = 83 + 425 - 458 \text{ meV at } 385 \text{ K.} \quad (6)$$

Thermochemical quantities for the electron are expressed using Boltzmann statistics for reasons laid out in the JANAF tables.<sup>19</sup> The net change in integrated heat capacity is 50 meV at 385 K. As it happens, the entropy and specific heat contributions practically cancel each other. The final result using these figures in Eq. (2) is  $\text{EA}(c\text{-C}_4\text{F}_8) = 631 \text{ meV}$ . (Other thermochemical quantities with these numbers are  $\Delta G^0 = -625 \text{ meV}$  and  $\Delta H^0 = -681 \text{ meV}$  at 385 K.) Similar analysis of all data for which optimum conditions obtain ( $\nu_a$  comparable to  $k_d$  and both larger than  $\nu_D$ ) give us an average value  $\text{EA}(c\text{-C}_4\text{F}_8) = 0.63 \pm 0.05 \text{ eV}$ . The uncertainty was determined by letting  $k_a$  and  $k_d$  take extreme values and including additional estimated uncertainty in the temperature. Errors in the calculated entropies and integrated heat capacities affect EA at the fraction-of-a-milli-electron-volt level.<sup>8</sup> Since EA has only a logarithmic dependence on the ratio of  $k_a$  to  $k_d$ , EA is rather insensitive to errors in these quantities. Accuracy in the temperature measurement is more important.

The results obtained from the present experiment [ $\text{EA}(c\text{-C}_4\text{F}_8) = 0.63 \pm 0.05 \text{ eV}$ ] and calculations [ $\text{G3}(\text{MP2})\text{EA}(c\text{-C}_4\text{F}_8) = 0.595 \text{ eV}$ ] imply that the high value reported by Hiraoka *et al.*<sup>4</sup> ( $1.05 \pm 0.10 \text{ eV}$ ) cannot be correct. It is supposed that the charge transfer equilibrium with SF<sub>6</sub> in that experiment does not actually reach equilibrium. The present result is the most accurate value of EA(*c*-C<sub>4</sub>F<sub>8</sub>) available. EA(*c*-C<sub>4</sub>F<sub>8</sub>) cannot be measured using anion photoelectron spectroscopy because of poor Franck-Condon overlap between the anion and neutral.<sup>20</sup> A very early tandem mass spectrometer measurement<sup>21</sup> gave EA(*c*-C<sub>4</sub>F<sub>8</sub>) =  $0.4 \pm 0.3 \text{ eV}$ , but the result should be disregarded because other EA results in the same paper have been proven incorrect by over 1 eV.

Hiraoka *et al.*<sup>4</sup> further stated that neutral *c*-C<sub>4</sub>F<sub>8</sub> has *D*<sub>4h</sub> symmetry, based on DFT calculations, though this conclusion was softened in a footnote. We repeated those calculations and find the puckered-ring *D*<sub>2d</sub> geometry to be correct, in agreement with the higher-level DFT calculations used in the present work and with the MP2 geometry optimization carried out as part of the G3(MP2) calculations. This finding is in agreement with the calculations of Mao *et al.*,<sup>22</sup> Winstead *et al.*,<sup>23</sup> and with the conclusions drawn from electron diffraction.<sup>24</sup> The identification of the point groups for the neutral and anion are important because of the effect of the rotational symmetry number on the entropy.

The  $k_a$  results reported here are lower than given in Ref. 1, though within error limits. At 298 K,  $k_a = 9.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ . We had earlier<sup>3</sup> obtained  $1.1 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ , but reanalyzed the data including an estimate of the detachment rate and found  $1.5 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ . We now know that the detachment rate at 298 K is too small to have any effect on the data (Fig. 2). We have checked flowmeter and gas pressure calibrations and believe that the

present  $k_a$  and  $k_d$  results are closer to being correct, especially as relates to the temperature measurement. The  $k_d$  results reported here compare well with those we gave earlier at a single temperature, provided the temperature is corrected as detailed in Sec. II. The Oak Ridge group has reported<sup>25</sup> values of  $k_a$  in the range  $9-12 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ . An early measurement of  $k_a = 1.2 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  was made by Bansal and Fessenden.<sup>26</sup> In contrast to these results for  $k_a$  is the much lower value obtained by Woodin *et al.*<sup>27</sup> at essentially zero pressure ( $k_a = 4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ) where no collisional stabilization occurs.

## V. CONCLUSIONS

Electron attachment rate constants  $k_a$  for  $(D_{2d}, ^1A_1)c\text{-C}_4\text{F}_8$  and electron detachment rate constants  $k_d$  for  $(D_{4h}, ^2A_{2u})c\text{-C}_4\text{F}_8^-$  have been measured over the 298–400 K temperature range (Table I). The value of  $k_a$  at 298 K is  $9.3 \pm 3.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , which implies an attachment efficiency of about 1 in every 40 collisions.<sup>28</sup> The value of  $k_d$  is too small to be measured at room temperature, but increases nearly exponentially to a value of  $1945 \pm 680 \text{ s}^{-1}$ . The equilibrium constant yields  $\text{EA}(c\text{-C}_4\text{F}_8) = 0.63 \pm 0.05 \text{ eV}$ , the most accurate determination of this quantity to date. G3(MP2) calculations yield  $\text{EA}(c\text{-C}_4\text{F}_8) = 0.595 \text{ eV}$ . These results imply that the  $c\text{-C}_4\text{F}_8^-/\text{SF}_6^-$  equilibrium experiments of Hiraoka *et al.*,<sup>4</sup> giving a higher EA, are incorrect. However, the  $c\text{-C}_4\text{F}_8^-/\text{O}_2^-$  equilibrium experiments of Hiraoka *et al.*,<sup>4</sup> giving a low EA, are consistent with the present work. The  $k_d$  measurements of Hiraoka *et al.* also imply a low value for  $\text{EA}(c\text{-C}_4\text{F}_8)$ .

Bond energies were also calculated for loss of F from  $c\text{-C}_4\text{F}_8$  and loss of F or  $\text{F}^-$  from  $c\text{-C}_4\text{F}_8^-$ . Dissociative electron attachment was found to be endothermic by at least 1.55 eV.

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